



DECLARATION

I, Yukiko HAYASHI, the translator of the attached document, do hereby certify that to the best of my knowledge and belief the attached document is a true English translation of Japanese Patent Application No. 2002-245932.

Signed, this ninth day of November, 2005

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[Title of the Invention] Dry Toner

[Scope of Claims]

[Claim 1] Dry toner comprising at least a toner binder, a
colorant, and wax, characterized in that an occupied area ratio
30 of the wax is between 5 and 40 % in an area from a surface of toner
particle to a 1 μ m inner area, according to observation by a
transmission electron microscope.

[Claim 2] The dry toner according to claim 1, characterized in

that an amount of wax existing in the toner particle in a portion outside one-half of a toner particle radius is 70 % by number or more relative to entire wax existing in the toner particle according to observation by a transmission electron microscope.

5 [Claim 3] The dry toner according to claim 1, characterized in that the wax is not exposed on the surface of the toner particle.

 [Claim 4] The dry toner according to claim 1, characterized in that 70 % by number or more of a dispersed wax particle dispersedly existing inside the toner particle has a diameter of 0.1 to 3 μm .

10 [Claim 5] The dry toner according to claim 1, characterized in that any one of or in combination of free fatty acid eliminated camauba wax, rice wax, and montan wax are used as the wax.

 [Claim 6] The dry toner according to claim 1, characterized in that modified polyester (i) is included as the toner binder.

15 [Claim 7] The dry toner according to claim 5, wherein the dry toner may be obtained by dissolving or dispersing a toner composite including the modified polyester (i) in an organic solvent, and then dispersing in an aqueous solvent.

 [Claim 8] The dry toner according to claim 5, wherein the dry
20 toner may be obtained by generating polyester having a urea bonding in a process of dissolving or dispersing a toner composite including a pre-polymer in the organic solvent, and then dispersing in the aqueous solvent.

 [Claim 9] The dry toner according to claim 5, characterized in
25 that the toner binder comprises unmodified polyester (ii) as well as the modified polyester (i), and that a weight ratio of the (i) to the (ii) is between 5/95 and 80/20.

 [Claim 10] The dry toner according to claim 1, characterized in that a peak molecular weight of the toner binder is 1000 to 10000.

30 [Claim 11] The dry toner according to claim 1, characterized in that glass transition temperature (T_g) of the toner binder is between 40 and 70 $^{\circ}\text{C}$.

 [Claim 12] The dry toner according to claim 1, characterized

in that a volume average particle diameter of the toner is between 3.0 and 8.0 μm , and a ratio of the volume average particle diameter to a number average diameter (D_n) D_v/D_n is between 1.00 and 1.20.

[Claim 13] The dry toner according to claim 1, characterized
5 in that an average circularity of the toner is between 0.93 and 1.00.

[Claim 14] An image forming apparatus for fixing a toner image on a transfer member by passing the transfer member between two rollers and thereby heating and fusing the toner image, wherein
10 surface pressure applied between the two rollers (roller load/contact area) is 1.5×10^5 Pa or less, the image forming apparatus characterized by using the toner according to any one of claims 1 through 13.

[Detailed Description of the Invention]

15 [0001]

[Technical Field of the Invention]

The present invention relates to toner for use in a developer for developing an electrostatic image in electrophotography, electrostatic recording, electrostatic printing, and so forth, and
20 an electrophotography development device using the toner. More specifically, the present invention relates to toner, a developer, a development device for electrophotography for use in a copier, a laser printer, a facsimile for plane paper, and so forth, using a direct or indirect electrophotographic development method.
25 Further, the present invention relates to a toner agent for electrophotography and an image forming apparatus (development device) for use in a full-color copier, a full-color laser printer, a full-color facsimile for plane paper using a direct or indirect electrophotographic multicolor development method.

30 [0002]

[Background Art]

A developer for use in electrophotography, electrostatic recording, electrostatic printing, and so forth, temporarily

adheres on an image carrier such as a photoconductor, for instance, on which an electrostatic image is formed in a development process. Then the developer is transferred from the photoconductor to a transfer medium such as transfer paper in a transfer process, and
5 is fixed on the transfer medium in a fixing process. As a developer for developing the electrostatic image formed on an latent image holding surface, a two-component type developer including a carrier and toner, and a one-component type developer which do not require the carrier (magnetic toner, non-magnetic toner) are known.

10 As dry toner used in the electrophotography, the electrostatic recording, the electrostatic printing, and so forth, toner formed of by melting and kneading a toner binder (binder resin) such as a styrene resin and polyester with a colorant, and then pulverizing a resulting mixture is conventionally used.

15 [0003]

After the dry toner is transferred on paper, and so forth, for development, the dry toner is fixed by heating and melting by using a heat roller. In this case, when temperature of the heat roller is too high, a problem (hot offset) that the toner excessively melts
20 and adheres on the heat roller occurs. In addition, when the temperature of the heat roller is too low, a problem arises in that the toner does not sufficiently melt, resulting in insufficient fixing. Accordingly, from a viewpoint of energy conservation and downsizing of a device such as a copier, there is a demand in toner
25 having higher temperature to cause the hot offset (excellent hot offset resistance) and low fixing temperature (excellent fixing characteristic at low temperature). In addition, the toner is required to have heat-resistant storage stability such that blocking of toner is not caused when the toner is stored or at ambient
30 temperature in a device. Particularly, in a full-color copier and a full-color printer, since glossiness and a color mixing property of an image is required, it is necessary for the toner to have lower melting viscosity. Consequently, a polyester toner binder

exhibiting sharp melting characteristic is used. However, hot offset is likely to occur with such toner. Accordingly, in a full-color device, silicone oil, and so forth, is conventionally applied on the heat roller. At the same time, an oil tank and an oil applying device are required in a method of applying silicone oil on the heat roller. Accordingly, the device becomes complex and large in size. In addition, with the method, the heat roller is caused to be deteriorated and maintenance per certain period is required. Further, it is unavoidable that oil adheres on copy paper, a film for an OHP (overhead projector), and so forth. Particularly in the OHP, there is a problem such that the adhered oil deteriorates a color tone.

[0004]

To prevent toner fusion without applying the oil on the heat roller, a method of adding wax in the toner is generally used. Releasing effect of the method is largely affected by a condition of dispersed wax in the binder. When the wax is compatible with the binder, a releasing characteristic of the wax may not be developed. The releasing characteristic of the wax may be improved only when the wax exist as a incompatible domain particle. When a dispersion diameter of the domain particle is too large, a ratio of wax existing adjacent to a surface of the toner particle relatively increases. Consequently, the toner exhibits an aggregation characteristic, lowering fluidity. Further, filming is caused due to the wax or a carrier transfers onto a photoconductor during long-term use. Accordingly, a problem such that an image with favorable quality is prevented from being achieved. In addition, in a case of color toner, color reproducibility and transparency are impaired. On the contrary, when the dispersion diameter is too small, the wax is excessively and finely dispersed and the releasing characteristic may not be sufficiently achieved. As described above, even though it is essential to control the dispersion diameter of the wax, an appropriate control method is

not yet found. Particularly, in a case of toner manufactured by a pulverization method, a significant factor in determining the dispersion diameter is sheer force of kneading during melting and kneading. A polyester resin which is often used for toner binder
5 in recent years is low in viscosity, and consequently, the shear force of kneading may not be applied. Accordingly, it is very difficult to control the dispersion diameter of the wax to obtain an adequate dispersion diameter.

In addition, another problem of the pulverization method is that
10 an amount of wax to be exposed on a surface may be increased because of the wax is likely to have a fracture surface.

[0005]

To achieve a high quality image, an attempt is made to improve toner by reducing a toner particle diameter or by narrowing a
15 particle size distribution. However, a form of a particle obtained with a conventional manufacturing method is amorphous. Consequently, the toner is further pulverized by being agitated with carrier in a development part in a machine, or by contact stress between the toner and a development roller, a toner supply roller,
20 a layer thickness regulation blade, a frictional charging blade, and so forth, when the toner is used as a one-component type developer. Accordingly, an extremely fine particle may be generated or a fluidizer is embedded on a surface of the toner. As a result, a phenomenon of deterioration of image quality occurs. In addition,
25 fluidity of the toner as a powder body is poor because of a shape of the toner particle. Accordingly, a large amount of the fluidizer is required and a filling rate of the toner into a toner bottle is low, becoming an obstacle factor to downsizing.

[0006]

30 Further, a transfer process of an image formed of multiple toner to make a full-color image from a photoconductor to a transfer medium or paper is becoming more complicated. Consequently, due to poor transferability of pulverized toner, and so forth, having an

amorphous shape, there is a problem such as a hollow defect in the transferred image or a large amount of toner for filling the hollow defect is consumed.

[0007]

5 Accordingly, demands for a high-quality image without a hollow defect and for lowering running cost by further improving transfer efficiency and reducing the amount of toner consumption are increasing. If the transfer efficiency is very good, a cleaning unit for removing untransferred toner from the photoconductor or
10 the transfer medium may not be required. This is because that an apparatus may be downsized and cost of the apparatus may be lowered. At the same time, there is an advantage that waste toner is reduced. To redeem a fault in the amorphous shape, various kinds of methods for producing spherical toner are invented.

15 [0008]

In the past, many studies are conducted to improve a toner characteristic. It is known that a releasing agent (wax) having a low softening point such as polyolefin is added in toner to improve fixing performance at low temperature and offset resistance.

20 Japanese Patent Application Laid-Open No. Hei6-295093, Japanese Patent Application Laid-Open No. Hei7-84401, and Japanese Patent Application Laid-Open No. Hei9-258471 propose toner including wax having a certain endothermic peak by DSC (differential scanning calorimetry). However, the fixing characteristic at low
25 temperature and the offset resistance of the toner are required to be further improved. In addition, it is necessary to improve developability.

[0009]

In addition, Japanese Patent Application Laid-Open No.
30 Hei5-341577, Japanese Patent Application Laid-Open No. Hei6-123999, Japanese Patent Application Laid-Open No. Hei6-230600, Japanese Patent Application Laid-Open No. Sho6-295093, Japanese Patent Application Laid-Open No. Hei6-324514, and Japanese Patent

Application Laid-Open No. Hei6-230600 disclose use of candelilla wax, higher fatty acid wax, higher alcohol wax, vegetable wax (carnauba, rice), montan ester wax, and so forth, as the releasing agent. However, the fixing characteristic at low temperature and the off set resistance of the toner are required to be further improved. In addition, it is necessary to improve the developability (charging characteristic) and durability of the toner. Generally, if the releasing agent having a low softening point as described above is added in the toner, fluidity of the toner decreases, resulting in lowering the developability and the transferability. In addition, the charging characteristic, the durability, and the storage stability are likely to be negatively affected.

[0010]

Japanese Patent Application Laid-Open No. Hei11-258934, Japanese Patent Application Laid-Open No. Hei11-258935, Japanese Patent Application Laid-Open No. Hei4-299357, Japanese Patent Application Laid-Open No. Hei4-337737, Japanese Patent Application Laid-Open No. Hei6-208244, and Japanese Patent Application Laid-Open No. Hei7-281478 propose toner including two or more kinds of releasing agents to enlarge a fixing area (non offset area). However, the toner still has a problem in uniform dispersion of the releasing agent in the toner particles.

[0011]

In addition, Japanese Patent Application Laid-Open No. Hei8-166686 proposes toner including a polyester resin and two types of offset inhibitors each having different acid values and softening points. However, the toner still has a problem in the developability.

In addition, Japanese Patent Application Laid-Open No. Hei8-328293 and Japanese Patent Application Laid-Open No. Hei10-161335 specify a dispersion diameter of wax within the toner. However, since a condition and a position inside the toner are not

defined, there is a case that sufficient releasing characteristic in fixing may not be obtained.

[0012]

Further, Japanese Patent Application Laid-Open No. 2001-305782
5 proposes toner in which a spherical wax particle is fixed on a surface of the toner. However, the wax existing on the toner surface decreases fluidity of the toner, lowering the developability and the transferability.

In addition, the charging characteristic, the durability, and
10 the storage stability are likely to be negatively affected. In addition, Japanese Patent Application Laid-Open No. 2002-26541 proposes a toner in which wax is included in a toner particle and the wax is locally located adjacent to a surface of the toner particle. However, there is a case that all of the offset resistance, the
15 storage stability, and the durability are insufficient.

[0013]

At the same time, toner is generally manufactured by a kneading and pulverization method. In the method, a heat plasticity resin is melted and kneaded with a pigment and further, if needed, with
20 a releasing agent or a charge control agent such as wax, then the resulting mixture is finely pulverized and further graded. In some cases, if needed, an inorganic or organic fine particle may be added on a surface of the toner particle to improve fluidity or cleaning ability. In a normal kneading and pulverization method, a shape
25 and surface structure of the toner are amorphous and subtly changes according to crushability of a material used and a condition of a pulverizing step. However, it is not easy to arbitrarily control the shape and the surface structure of the toner. In addition, it is difficult to further narrow a particle size distribution of the
30 toner due to limiting ability in grading, and because it may increase cost. In addition, as to an average particle diameter of the particle size distribution in the toner, it is a significant task to control the average particle diameter to have a small diameter,

particularly a 6 μ m or less, from a viewpoint of yield, productivity, and cost.

[0014]

[Problems to be Solved]

5 (1) It is an object of the present invention to provide toner which has improved fixing ability at low temperature and offset resistance with low electric power consumption, forms a high quality toner image, and has long-term excellent storage stability.

(2) It is another object of the present invention to provide toner
10 which may achieve a high quality image with a wide fixing area.

(3) Further, it is also another object of the present invention, in a case of color toner, to provide toner excellent in glossiness and hot offset resistance.

(4) Furthermore, it is also another object of the present
15 invention to provide toner capable of forming a high-resolution image.

(5) Furthermore, it is also another object of the present invention to provide an image forming apparatus using the toner.

[0015]

20 [Means for Solving the Problems]

The inventors of the present invention achieved the present invention as a result of an intensive study to develop toner having a wide fixing area, excellent particle fluidity and transferability in a case of toner having a small particle diameter, excellent
25 heat-resistant storage stability, fixing characteristic at low temperature, and hot offset resistance. Particularly, the study is done to develop dry toner which has excellent glossiness when used in a full-color copier, and so forth, and does not require application of oil to a hear roller.

30 [0016]

More specifically, according to the present invention, a dry toner method and an image forming apparatus as described below may be provided.

(1) Dry toner comprising at least a toner binder, a colorant, and wax, characterized in that an occupied area ratio of the wax is between 5 and 40 % in an area from a surface of toner particle to a 1 μ m inner area, according to observation by a transmission
5 electron microscope.

(2) The dry toner according to (1), characterized in that an amount of wax existing in the toner particle in a portion outside one-half of a toner particle radius is 70 % by number or more relative to entire wax existing in the toner particle, according to
10 observation by a transmission electron microscope.

(3) The dry toner according to (1), characterized in that the wax is not exposed on the surface of the toner particle.

(4) The dry toner according to (1), characterized in that 70 % by number or more of a dispersed wax particle dispersedly existing
15 inside the toner particle has a diameter of 0.1 to 3 μ m.

(5) The dry toner according to (1), characterized in that any one of or in combination of free fatty acid eliminated camauba wax, rice wax, and montan wax are used as the wax.

(6) The dry toner according to (1), characterized in that
20 modified polyester (i) is included as the toner binder.

(7) The dry toner according to (6), wherein the dry toner may be obtained by dissolving or dispersing a toner composite including the modified polyester (i) in an organic solvent, and then dispersing in an aqueous solvent.

25 (8) In (6), the dry toner according to (5), wherein the dry toner may be obtained by generating polyester having a urea bonding in a process of dissolving or dispersing a toner composite including a pre-polymer in the organic solvent, and then dispersing in the aqueous solvent.

30 (9) The dry toner according to (6), characterized in that the toner binder includes unmodified polyester (ii) as well as the modified polyester (i), and that a weight ratio of the (i) to the (ii) is between 5/95 and 80/20.

(10) The dry toner according to (1), characterized in that a peak molecular weight of the toner binder is 1000 to 10000.

(11) The dry toner according to (1), characterized in that glass transition temperature (Tg) of the toner binder is between 40 and 70 °C.

(12) The dry toner according to (1), characterized in that a volume average particle diameter of the toner is between 3.0 and 8.0 μm , and a ratio of the volume average particle diameter to a number average diameter (Dn) D_v/D_n is between 1.00 and 1.20.

(13) The dry toner according to (1), characterized in that an average circularity of the toner is between 0.93 and 1.00.

(14) An image forming apparatus for fixing a toner image on a transfer member by passing the transfer member between two rollers and thereby heating and fusing the toner image, wherein surface pressure applied between the two rollers (roller load/contact area) is 1.5×10^5 Pa or less, the image forming apparatus characterized by using the toner according to any one of (1) through (13).

[0017]

The inventors of the present invention found toner in which a wax particle having an appropriate particle diameter is stably dispersed and a manufacturing method of the toner. With the method, a negative adsorption occurs on a connection part of the polar group of the toner binder (particularly a modified polyester) at an interface of the wax. It is assumed that this leads to stable dispersion of the wax having low polarity. Further, particularly in a method of obtaining a toner particle by dissolving or dispersing a toner composition in an organic solvent, and dispersing the toner particle in an aqueous solvent, the connection part having a high polarity slightly exhibits hydrophilicity. However, an effect such that a wax particle is prevented from being exposed to a surface is achieved.

[0018]

When the wax dispersedly exists in an interior portion of the

toner particle, and an occupied area ratio of the wax is between 5 and 40 % in an area from a surface of toner particle to a 1 μ m inner area, particularly when an amount of wax existing in the toner particle from a vicinity of the toner particle surface is 70 % by number or more relative to the entire wax existing in the toner particle, the wax may come out sufficiently during fixing. As a result, fixing not requiring fixing oil, what is called oilless fixing, may be achieved particularly in glossy color toner. Further, since an amount of wax existing on the surface of the toner particle is small under a normal usage condition, the toner has excellent durability, stability, and storage stability.

[0019]

When an occupied area ratio of the wax is less than 5 % in an area from a surface of toner particle to a 1 μ m inner area, hot offset resistance becomes insufficient. In addition, when the occupied area ratio of the wax is more than 40%, it may result in insufficient thermal resistance and durability.

Further, distribution of a particle diameter of the dispersed wax existing in the toner particle according to the present invention is that 70 % by number or more of the wax particles have a diameter of 0.1 to 3 μ m, and preferably that 70 % by number or more of the wax particles have a diameter of 1 to 2 μ m. When a large number of wax particles have a diameter of less than 0.1 μ m, a releasing characteristic may not be sufficiently achieved. In addition, when a large number of wax particles have a diameter of more than 3 μ m, aggregation of toner particles may occur, resulting in lowered fluidity and occurrence of filming. Further, in a case of color toner, color reproducibility and glossiness are significantly impaired.

[0020]

In the present invention, a diameter of the dispersed wax particle is defined as a largest diameter of the dispersed wax particle. The diameter of the dispersed wax is measured as follows.

Specifically, the toner particle is embedded in an epoxy resin and is then ultra-thinly sliced. The toner particle is dyed with ruthenium tetroxide. Thereafter, a cross-section surface of the ultra-thinly sliced toner is observed under a transmission electron microscope (TEM) at a magnification of 10000, and photographs of the toner are taken. Twenty pictures (20 particles of the toner) are subjected to image evaluation. Thus a condition of dispersed wax is observed and the diameter of the dispersed wax is measured.

[0021]

An occupied area ratio of the wax in an area from a surface of toner particle to a 1 μm inner area from the surface is obtained by calculating an existence ratio of the wax from a surface of toner particle to a 1 μm inner area in an area ratio.

The wax not existing on the toner surface but existing adjacent to the toner surface is defined, from the pictures taken as described above, as the toner existing more toward the surface of the toner than toward a curved line connecting the surface of the toner particle and a middle portion of the radius (middle point on bisected radius) (however, when wax exists on a curved line formed of the surface of the toner particle and a middle portion of the radius the wax is determined to exist on a centric portion).

[0022]

Further, an endothermic peak of the wax measured by a differential scanning calorimeter (DSC) when temperature is increasing may be between 65 and 115 $^{\circ}\text{C}$ in terms of fixing of toner at low temperature. However, when a melting point of the wax is 65 $^{\circ}\text{C}$ or below, fluidity of the toner tends to be poor. When the melting point of the wax is higher than 115 $^{\circ}\text{C}$, fixing ability of the toner tends to be poor.

An object is achieved when the wax immediately comes out on the surface of the toner particle during fixing. Wax having a high acid value lowers its function as a releasing agent. To secure the function as the releasing agent, the wax is preferably free fatty acid eliminated carnauba wax, rice wax, montan wax, or ester wax

each having an acid value of 5 KOHmg/g or less.

[0023]

Modified polyester in the present invention refers to a polyester resin having a bonding other than an ester bonding in the polyester, or a polyester resin having a structurally different resin component in the polyester with a covalent bonding, an ionic bonding, and so forth. The example of the modified polyester includes polyester of which terminal is reacted with other than an ester bonding. Specifically, the polyester in which a functional group capable of reacting with an acid radical and a hydroxyl group, for example an isocyanate group, and so forth, is introduced to the terminal of the polyester and thereafter the terminal are further reacted with an active hydrogen compound so as to modify the terminal of the polyester.

[0024]

A favorable example of the modified polyester used in the present invention (i) is a reactant of a polyester pre-polymer having an isocyanate group (A) and amines (B), and so forth. Examples of the polyester pre-polymer having the isocyanate group (A) may include a reactant that is a polycondensation product of polyol (1) and poly carboxylic acid (2), and also a reactant of the polyester having an active hydrogen compound and polyisocyanate (3). Examples of the active hydrogen contained in the polyester may include a hydroxyl group (an alcoholic hydroxyl group and a phenolic hydroxyl group), an amino group, a carboxy group, a mercapto group, and so forth. Of these, the alcoholic hydroxyl group is preferable.

[0025]

Examples of the polyol (1) include diol (1-1) and polyol having 3 or more valences (1-2). They are suitably used singly or in combination of the diol (1-1) and a small amount of the polyol (1-2). Examples of the diol (1-1) may include alkylene glycol (ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butane diol, 1,6-hexane diol, and so forth), alkylene ether glycol

(diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, poly tetramethylene ether glycol, and so forth), alicyclic diol (1,4-cyclohexane dimethanol, hydrogenated bisphenol A, and so forth), bisphenols (bisphenol A, bisphenol F, bisphenol S, and so forth), an adduct of the alicyclic diol with alkylene oxide (ethylene oxide, propylene oxide, butylene oxide, and so forth) an adduct of the bisphenols with alkylene oxide (ethylene oxide, propylene oxide, butylene oxide, and so forth). Of these, the alkylene glycol having carbon atoms of between 2 and 12 and the adduct of the bisphenols with the alkylene oxide are preferable. A combination of the adduct of the bisphenols with the alkylene oxide and the alkylene glycol having carbon atoms of between 2 and 12 is particularly preferable. Examples of the polyol having 3 or more valences (1-2) may include polyhydric aliphatic alcohol having 3 to 8 valences or more (glycerine, trimethylolethane, trimethylolpropane, pentaerythritol, sorbitol, and so forth), phenols having 3 or more valences (trisphenol PA, phenol novolak, cresol novolak, and so forth), and an adduct of the polyphenol having 3 or more valences with alkylene oxide.

[0026]

Examples of polycarboxylic acid (2) may include dicarboxylic acid (2-1) and polycarboxylic acid having 3 or more valences (2-2). The dicarboxylic acid (2-1) may suitably be used singly or in a combination with a small amount of the polycarboxylic acid (2-2). Examples of the dicarboxylic acid (2-1) may include alkylene dicarboxylic acid (succinic acid, adipic acid, sebacic acid, and so forth), alkenylene dicarboxylic acid (maleic acid, fumaric acid, and so forth), and aromatic dicarboxylic acid (phthalic acid, isophthalic acid, terephthalic acid, naphthalene dicarboxylic acid, and so forth). Of these, the alkenylene carboxylic acid having carbon atoms of between 4 and 20 and the aromatic dicarboxylic acid having carbon atoms of between 8 and 20 are preferable. Examples

of the polycarboxylic acid having 3 or more valences (2-2) may include aromatic polycarboxylic acid having carbon atoms of between 9 and 20 (trimellitic acid, pyromellitic acid, and so forth). As the polycarboxylic acid (2), furthermore, acid anhydride of the above listed examples or lower alkyl ester (methyl ester, ethyl ester, isopropyl ester, and so forth) may be used to react with the polyol (1).

[0027]

A ratio of the polyol (1) to the polycarboxylic acid (2) is, in terms of equivalent ratio of hydroxyl group [OH] to carboxyl group [COOH] ($[OH]/[COOH]$), generally about 2/1 to about 1/1, preferably 1.5/1 to 1/1, and more preferably 1.3/1 to 1.02/1.

[0028]

Examples of the polyisocyanate (3) may include aliphatic polyisocyanate (tetramethylene diisocyanate, hexamethylene diisocyanate, 2,6-diisocyanate methylcaproate, and so forth), alicyclic polyisocyanate (isophorone diisocyanate, cyclohexylmethane diisocyanate, and so forth), aromatic diisocyanate (tolylene diisocyanate, diphenylmethane diisocyanate, and so forth), aromatic aliphatic diisocyanate ($\alpha, \alpha, \alpha', \alpha'$ -tetramethylxylene diisocyanate, and so forth), isocyanurates; a block-compound in which the polyisocyanate is blocked with phenol derivatives, oxime, caprolactone, and so forth; and a combination of two or more of the above ingredients.

[0029]

A ratio of the polyisocyanate (3) is, in terms of equivalent ratio of isocyanate group [NCO] to hydroxyl group [OH] ($[NCO]/[OH]$), generally about 5/1 to about 1/1, preferably 4/1 to 1.2/1, and more preferably 2.5/1 to 1.5/1. When the ratio $[NCO]/[OH]$ is more than 5, fixing ability at low temperature is impaired. When a mole ratio of [NCO] is less than 1, the urea content in the modified polyester becomes low hence hot offset resistance is impaired. In the pre-polymer having an isocyanate group at the terminal thereof (A),

a content of polyisocyanate (3) composition is generally about between 0.5 and about 40 % by weight, preferably 1 to 30 % by weight, and more preferably between 2 and 20 % by weight. When the content of the polyisocyanate (3) composition is less than 0.5 % by weight, not only impairing hot offset resistance, but it is disadvantageous in terms of having heat-resistant storability together with fixing ability at low temperature. When the content is more than about 40 % by weight, on the other hand, the fixing ability at low temperature is impaired.

[0030]

A number of isocyanate groups contained in the pre-polymer having the isocyanate group (A) per molecular is generally one or more, preferably between 1.5 and 3 in average, and more preferably between 1.8 and 2.5 in average. When the number of isocyanate group per molecular is less than one, the molecular weight of urea-modified polyester becomes low, and therefore, hot offset resistance is impaired.

[0031]

Examples of the amines (B) may include diamine (B1), polyamine having 3 or more valences (B2), amino alcohol (B3), amino mercaptan (B4), amino acid (B5), and a block compound in which the amino group of B1 to B5 is blocked (B6). Examples of the diamine (B1) may include aromatic diamine (phenylene diamine, diethyltoluene diamine, 4,4'-diaminophenylmethane, and so forth), alicyclic diamine (4,4'-diamino-3,3'-dimethyldicyclohexylmethane, diamine cyclohexane, isophorone diamine, and so forth), and aliphatic diamine (ethylene diamine, tetramethylene diamine, hexamethylene diamine, and so forth). Examples of the polyamine having 3 or more valences may include ethylene triamine, triethylene tetramine. Examples of the amino alcohol (B3) may include ethanolamine, hydroxyethylaniline, and so forth. Examples of the amino mercaptan (B4) may include aminomethylmercaptan, aminopropylmercaptan, and so forth. Examples of amino acid (B5) may include amino propionic

acid, amino capric acid, and so forth. Examples of the block compound in which the amino group of B1 to B5 is blocked (B6) may include a ketimine compound, an oxazoline compound, and so forth obtained from the amines and ketones of B1 to B5 (acetone, methylethylketone, methylbutylketone, and so forth. Of the amines (B) listed above, the diamine B1 and a combination of the diamine B1 and a small amount of polyamine B2 are preferable.

[0032]

Further, the molecular weight of the urea-modified polyester may be adjusted by using an elongation inhibitor, if needed. The elongation inhibitor may include monoamine (diethyl amine, dibutyl amine, butyl amine, lauryl amine, and so forth) and a block compound, and so forth, in which the monoamine is blocked (ketimine compound).

[0033]

The ratio of the amines (B) is, in terms of equivalent ratio of isocyanate group [NCO] in the pre-polymer having an isocyanate group (A) to amino group [NHx] in the amines (B) ($[NCO]/[NHx]$), generally between 1/2 and 2/1, preferably between 1.5/1 and 1/1.5, and more preferably between 1.2/1 and 1/1.2. When the equivalent ratio $[NCO]/[NHx]$ is more than 2 or less than 1/2, the molecular weight of the urea-modified polyester becomes low, therefore, the hot offset resistance is impaired. In the present invention, the urea-modified polyester (i) may contain urethane bondings together with urea bondings. The mole ratio of an urea bonding content to an urethane bonding content is generally 100/0 to 10/90, preferably 80/20 to 20/80, and more preferably between 60/40 and 30/70. When the mole ratio of the urea bonding content is less than 10, the hot offset resistance is impaired.

[0034]

The urea-modified polyester (u) used in the present invention is manufactured by a one-shot method or a pre-polymer method. The weight average molecular weight of the urea-modified polyester (u) is generally 10,000 or more, preferably between 20,000 and

10,000,000, and more preferably between 30,000 and 1,000,000. When the above range is attained, the peak molecular weight of the urea-modified polyester (u) is between 1,000 and 10,000. When the peak molecular weight is less than 1,000, an elongation reaction
5 does not easily occur and elasticity of the toner is low, consequently, the hot offset resistance is impaired. When the peak molecular weight is 10,000 or more, the fixing ability is impaired and problems related to manufacturing may occur in formation of particles or pulverization, for instance. The number average
10 molecular weight of the urea-modified polyester is not particularly limited, especially when unmodified polyester (ii) is used in combination with the urea-modified polyester as described later, and any number average molecular weight may be used to obtain the above-mentioned range of the weight average molecular weight. In
15 a case of the urea-modified polyester (u) is used singly, the number average molecular weight is generally 20,000 or less, preferably 1,000 to 10,000, and more preferably 2,000 to 8,000. When the number average molecular weight is more than 20,000, fixing ability at low temperature and glossiness of toner used for a full-color
20 apparatus are impaired.

[0035]

In the present invention, not only singly, but the polyester modified by a urea bonding (u) is used in combination with an unmodified polyester (ii) as a toner binder resin. It is more
25 preferable to use the urea-modified polyester together with the unmodified polyester (ii) than to use the urea-modified polyester singly. This is because when the unmodified polyester is used, the fixing ability at low temperature and the glossiness of the toner when the toner is used in the full-color apparatus are improved.
30 Examples of the unmodified polyester (ii) may include a polycondensation product of the polyol (1) and the polycarboxylic acid (2) having an identical polyester composition of the urea-modified polyester (u), just as similar to the favorable

urea-modified polyester (u). In addition, the unmodified polyester (ii) may also be polyester which is modified by a chemical bonding other than an urea bonding, for instance, the polyester may be modified with an urethane bonding. It is preferable that at least a part of the (u) and the (ii) is compatible from a viewpoint of the low temperature fixing ability and the hot offset resistance. Accordingly, it is preferred that the (ii) has a similar component to the polyester component of the (u). The weight ratio of the (u) to the (ii), when the (ii) is contained together with the (u), generally 5/95 to 80/20, is preferably 5/95 to 30/70, and more preferably 7/93 to 20/80. When the weight ratio of the (u) to the (ii) is less than 5 %, not only the hot offset resistance is impaired, but also it is difficult to obtain heat-resistant storability together with low temperature fixing ability.

[0036]

The peak molecular weight of the (ii) is generally between 1,000 and 10,000, preferably between 2,000 and 8,000, and more preferably between 2,000 and 5,000. When the peak molecular weight of the (ii) is less than 1,000, heat-resistant storage stability is impaired. When the peak molecular weight of the (ii) is more than 10,000, low temperature fixing ability is impaired. The hydroxyl value of the (ii) is preferably 5 or more, more preferably between 10 and 120, and further preferably between 20 and 80. When the hydroxyl value the modified polyester is less than 5, it is difficult to obtain heat resistance storage stability together with fixing ability at low temperature. The acid value of the (ii) is between 1 and 5, and preferably between 2 and 4. Since the wax having a high acid value is used as wax, it is preferable to use a resin having a low acid value as a binder since the binder may lead to charging or high volume resistivity. Thus the toner formed from such wax and binder is suitable for a two-component toner.

[0037]

A glass transition point (T_g) of the toner binder used in the

present invention is generally 50 °C to 70 °C, and preferably 55 °C to 65 °C. When the glass transition point (Tg) of the toner binder is less than 50 °C, heat resistant storage stability is impaired. When the glass transition point (Tg) of the toner binder is more than 70 °C, low temperature fixing ability becomes insufficient. By containing the urea-modified polyester resin, the toner according to the present invention exhibits excellent heat-resistant storage stability, even when the glass transition point of the toner binder is low, with comparison to publicly-known polyester toner.

[0038]

As a colorant used in the present invention, all of publicly-known dyes and pigments may be used. For instance, carbon black, nigrosine dyes, black iron oxide, Naphthol Yellow S, Hansa Yellow (10G, 5G, G), cadmium yellow, yellow iron oxide, yellow ochre, chrome yellow, Titan Yellow, Polyazo Yellow, Oil Yellow, Hansa Yellow (GR, A, RN, R), Pigment Yellow L, Benzidine Yellow (G, GR), Permanent Yellow (NCG), Vulcan Fast Yellow (5G, R), Tartrazine Lake, Quinoline Yellow Lake, anthracene yellow BGL, isoindolinone yellow, red oxide, red lead oxide, red lead, cadmium red, cadmium mercury red, antimony red, Permanent Red 4R, Para Red, Fire Red, parachlorororthonitroaniline red, Lithol Fast Scarlet G, Brilliant Fast Scarlet, Brilliant Carmine BS, Permanent Red (F2R, F4R, FRL, FRLl, F4RH), Fast Scarlet VD, Vulcan Fast Rubine B, Brilliant Scarlet G, Lithol Rubine GX, Permanent Red F5R, Brilliant Carmine 6B, Pigment Scarlet 3B, Bordeaux 5B, Toluidine Maroon, Permanent Bordeaux F2K, Helio Bordeaux BL, Bordeaux 10B, BON Maroon Light, BON Maroon Medium, eosine lake, Rhodamine Lake B, Rhodamine Lake Y, Alizarine Lake, Thioindigo Red B, Thioindigo Maroon, Oil Red, quinacridone red, Pyrazolone Red, Polyazo Red, Chrome Vermilion, Benzidine Orange, Perynone Orange, Oil Orange, cobalt blue, cerulean blue, Alkali Blue Lake, Peacock Blue Lake, Victoria Blue Lake, metal-free phthalocyanine blue, Phthalocyanine Blue, Fast

Sky Blue, Indanthrene Blue (RS, BC), indigo, ultramarine blue, Prussian blue, Anthraquinone Blue, Fast Violet B, Methyl Violet Lake, cobalt violet, manganese violet, dioxazine violet, Anthraquinone Violet, chrome green, zinc green, chromium oxide, viridian, emerald green, Pigment Green B, Naphthol Green B, Green Gold, Acid Green Lake, Malachite Green Lake, Phthalocyanine Green, Anthraquinone Green, titanium oxide, zinc oxide, and lithopone, and mixtures thereof may be used. The content of the colorant is 1 to 15 % by weight, and preferably 3 to 10% by weight, relative to the total weight of the toner.

[0039]

The colorant for use in the present invention may be used as a master batch which is combined with a resin. Such binder resin used for the manufacturing of the master batch or in kneading with the master batch may include, in addition to the above-mentioned modified and unmodified polyester resins, polymers of styrene and substituted styrenes such as polystyrene, poly-p-chlorostyrene, polyvinyl toluene, and so forth, styrene copolymers such as styrene-p-chlorostyrene copolymer, styrene-propylene copolymer, styrene-vinyltoluene copolymer, styrene-vinylnaphthalene copolymer, styrene-methyl acrylate copolymer, styrene-ethyl acrylate copolymer, styrene-butyl acrylate copolymer, styrene-octyl acrylate copolymer, styrene-methyl methacrylate copolymer, styrene-ethyl methacrylate copolymer, styrene-butyl methacrylate copolymer, styrene-methyl α -chloromethacrylate copolymer, styrene-acrylonitrile copolymer, styrene-vinyl methyl ketone copolymer, styrene-butadiene copolymer, styrene-isoprene copolymer, styrene-acrylonitrile-indene copolymer, styrene-maleic acid copolymer, styrene-maleic ester copolymer, and so forth, polymethyl methacrylate, polybutyl methacrylate, polyvinyl chloride, polyvinyl acetate, polyethylenes, polypropylenes, polyesters, epoxy resins, epoxy polyol resins, polyurethanes, polyamides, polyvinyl butyral, polyacrylic acid

resin, rosin, modified rosin, terpene resins, aliphatic or alicyclic hydrocarbon resins, aromatic petroleum resins, chlorinated paraffin, paraffin wax, and so forth. Each of these may be used singly or in combination of two or more.

5 [0040]

The master batch according to the present invention may be obtained by mixing and kneading a resin for the master batch and the colorant with high shear force. In this case, to improve interaction between the colorant and the resin, an organic solvent may be used. In addition, the master batch is preferably prepared by a flushing method. In the flushing method, water-based paste containing the colorant and water is mixed and kneaded with the resin and an organic solvent so that the colorant moves towards the resin, and that the water and a component of the organic solvent are removed. According to the method, a wet cake containing the colorant may also be preferably used as it is, that is, without drying. The materials are preferably mixed and kneaded using a triple roll mill and other high-shear dispersing devices.

[0041]

20 The toner according to the present invention may contain a charge control agent, if needed. As the charge-controlling agent, all of publicly-known charge-controlling agent may be used. Examples may include a nigrosine dye, a triphenylmethane dye, a chromium-containing metal complex dye, a molybdcic acid chelate pigment, a rhodamine dye, an alkoxyamine, a quaternary ammonium salt (including fluorine-modified quaternary ammonium salt), alkylamide, a simplex or a compound of phosphorus, a simplex or a compound of tungsten, a fluorine-containing activator, a metallic salt of salicylic acid, a metallic salt of a salicylic acid derivative, and so forth. Specific examples thereof are BONTRON 03 of a nigrosine dye, BONTRON P-51 of a quaternary ammonium salt, BONTRON S-34 of a metal containing azo dye, E-82 of an oxynaphthoic acid metal complex, E-84 salicylic acid metal complex, E-89 of a

phenol condensation product (manufacture by Orient Chemical Industries, Ltd.), TP-302 and TP-415 of molybdenum complex of quaternary ammonium salt (manufactured by Hodoya Chemical Co., Ltd.), Copy Charge PSY VP2038 of a quaternary ammonium salt, Copy
5 Blue PR of a triphenyl methane derivative, Copy Charge NEG VP2036 and Copy Charge NX VP434 of a quaternary ammonium salt (manufactured by Hoechst Japan Ltd.), LRA-901, and LR-147 of a boric complex (manufactured by Japan Carlit Co., Ltd.); copper phthalocyanine, perylene, quinacridone, azo dyes, polymeric compounds having a
10 functional group such as a sulfonic group, a carboxyl group, a quaternary ammonium salt, and so forth.

[0042]

An amount of the charge control agent used in the present invention is not particularly limited and may be determined
15 according to a type of the resin, whether any additive is used according to need, and a method of manufacturing the toner including a dispersion method. Suitable amount of the charge control agent to be used is preferably between 0.1 and 10 parts by weight, and more preferably between 0.2 and 5 parts by weight, relative to 100
20 parts by weight of the binder resin. When the amount of the charge control agent is more than 10 parts by weight, the charging ability of the toner becomes excessively large. Consequently, the effect of the main charge control agent is impaired, electrostatic attraction between the toner and the developing roller is
25 excessively increased, fluidity of the developer is decreased, and the image density is decreased. The charge control agent and the releasing agent may be melted and kneaded together with the master batch and the resin, and may also be added when the ingredients are melted and dispersed in an organic solvent.

30 [0043]

An external additive for supplementing fluidity, developability, and a charging characteristic of a color particle achieved in the present invention may be used. As the external additive, an

inorganic fine particle may be preferably used. A primary particle diameter of the inorganic particle is preferably between 5 and 2 μm , and more preferably between 5 and 500 $\text{m}\mu$. The specific surface the inorganic particle in terms of BET method is preferably between 20 and 500 m^2/g . The content of the inorganic particle is preferably between 0.01 and 5 % by weight, and more preferably between 0.01 and 2.0 % by weight, relative to the total weight of the toner. Specific examples of the inorganic toner may include silica, aluminum, titanium oxide, barium titanate, magnesium titanate, calcium titanate, strontium titanate, zinc oxide, tin oxide, quartz sand, clay, mica, wollastonite, diatomaceous earth, chromium oxide, cerium oxide, red iron oxide, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium carbonate, calcium carbonate, silicon carbide, silicon nitride, and the like.

[0044]

Another examples of the external additive may include polymeric particles such as polystyrene formed of soap-free emulsion polymerization, suspension polymerization, and dispersion polymerization; copolymers of methacrylic ester and acrylic ester; polycondensation thermosetting resins such as silicone, benzoguanamine, and nylon.

[0045]

A surface treatment may be suitably performed on such a plasticizer to improve hydrophobicity and to prevent deteriorating fluidity and charging characteristic even in a high humidity environment. Favorable surface treatment agents are may include a silane coupling agent, a silylation reagent, a silane coupling agent having an alkyl fluoride group, an organic titanate coupling agent, an aluminium coupling agent, silicone oil, modified silicone oil, and so forth.

A cleaning agent for removing a developer remained a photoconductor or on a primary transfer medium after transfer may include, for instance, zinc stearate, calcium stearate, fatty acid

metal salt such as stearic acid, polymeric particles formed of soap-free emulsion polymerization such as a polymethyl methacrylate particle, a polystyrene particle, and so forth. The polymeric particles preferably have a relatively narrow particle diameter distribution and a volume average particle diameter of 0.01 to 1 μm .

[0046]

A production method of dry r according to the present invention is described in detail as follows.

10 A toner binder may be manufactured according to a following method, for instance. Polyol (1) and polycarboxylic acid (2) are heated at temperature between 150 and 280 °C under the presence of a publicly-known esterification catalyst such as tetrabuthoxytitanate, dibutyl tin oxide, and so forth. Thereafter, 15 the mixture is decompressed, if needed, while generated water in a course of decompressing is removed, so as to yield polyester having a hydroxyl group. Then the obtained polyester having a hydroxyl group is reacted with polyisocyanate (3) at temperature between 40 and 140 °C so as to yield a pre-polymer having an isocyanate group 20 (A). Further, (A) is reacted with (B) at temperature between 0 and 140 °C so as to yield polyester modified with a urea bonding. When (3) is reacted, and when (A) is reacted with (B), a solvent may be used, if needed. Usable solvents are, for instance, solvents which are inactive with the isocyanate (3), such as aromatic 25 solvents (toluene, xylene, and so forth), ketones (acetone, methylethylketone, methylisobutylketone, and so forth), esters (ethyl acetate, and so forth), amides (dimethylformamide, dimethylacetamide, and so forth), and ethers (tetrahydrofuran, and so forth). In a case that the polyester unmodified with an urea bonding (ii) is used in a combination with the urea-modified 30 polyester (u), (ii) is produced in a same manner as the polyester having a hydroxyl group, and then (ii) is dissolved and mixed into a solution after the completion of the reaction of (u).

The dry toner may be manufactured by a following method but is not to be considered limited thereto.

[0047]

When preparing a developer, the above-mentioned inorganic particles such as a hydrophobic silica particle may be added in order to improve fluidity, storage stability, developability, and transferring ability of the developer. The external additive is mixed by using a regular powder mixer. However, it is preferable to use the mixer that equips a jacket, and so forth, and is capable of controlling interior temperature. In order to modify the negative charging state given to the external additive, it may be added in middle of the process or gradually during a process. The number of revolution, rotating speed, time and temperature may of course be changed. At first, a strong load may be given followed by a relatively weak load, or a reverse may be done.

[0048]

Examples of mixing devices may include a V-shaped mixer, a rocking mixer, a Redige mixer, a Nauta mixer, a Henschel mixer, and so forth.

[0049]

The toner according to the present invention may be produced by dissolving or dispersing a component of the toner to an organic solvent and dispersing the solvent to an aqueous medium. As the aqueous medium in the present invention, water is used singly, or in combination with a solvent mixable with water. Examples of the solvent mixable with water may include alcohols (methanol, isopropanol, ethylene glycol, and so forth), dimethyl formamide, tetrahydrofuran, cellosolves (methylcellosolve, and so forth), lower ketones (acetone, methylethylketone, and so forth).

[0050]

To obtain a toner particle, dispersion formed of pre-polymer having an isocyanate group (A) may be reacted with (B) in an aqueous medium, or already produced urea-modified polyester (u) may be used. As a method of stably forming dispersion formed of the urea-modified

polyester (u) or the pre-polymer (A) in an aqueous medium, a method of adding a component of a toner material such as the urea-modified polyester (u) or the pre-polymer (A) in the aqueous medium, and dispersing the urea-modified polyester (u) or pre-polymer (A) using shear force may be included. The pre-polymer (A) and other toner components such as a colorant, a colorant master batch, a releasing agent, a charge control agent, an unmodified polyester resin (hereinafter referred to a toner raw material), may be mixed together when the dispersion is formed in an aqueous medium. However, it is more preferable that the toner raw materials are mixed together, followed by adding the mixture of the toner raw materials to the aqueous medium so as to disperse. Moreover, other toner components such as the colorant, the releasing agent, the charge control agent, and so forth, are not necessarily to be mixed when forming the particle in an aqueous medium, but may be added to the particle after the particle is formed. For example, the particle is formed without including a colorant, and then the colorant is added by a conventional dyeing method.

[0051]

The method of dispersing is not particularly limited, but conventional apparatuses of low-speed shearing, high-speed shearing, frictioninig, high pressure jet, ultrasonic wave, and so forth, may be used. Of these, the high-speed shearing apparatus is preferable in order to control a particle diameter of dispersion in a range of between 2 m and 20 μ m. There is no limitation on a number of rotation when the high-speed shearing apparatus is used, but the number of rotation is generally between 1,000 and 30,000 rpm, and preferably between 5,000 and 20,000 rpm. Dispersion time is, when a batch mixer is used, generally between 0.1 and 5 minutes, though it is not limited thereto. Temperature during dispersing is generally between 0 and 150 °C (under pressure), and preferably between 40 and 98 °C. High temperature is more preferable from viewpoints of low viscosity of dispersion formed of the

urea-modified polyester (u) or the pre-polymer (A), and dispersibility.

[0052]

An usage amount of the aqueous medium is generally between 50
5 and about 20,000 parts by weight, and preferably between 100 and
1,000 parts by weight, relative to 100 parts by weight of the toner
composition including the urea-modified polyester (u) or the
pre-polymer (A). When the usage amount is less than 50 parts by
weight, the dispersibility of the toner composition is poor and
10 a toner particle with a predetermined particle diameter may not
be achieved. When the usage amount is more than 20,000 parts by
weight, it is not economical. A dispersing agent may also be used,
if needed. It is preferable to use the dispersing agent from a
viewpoint of a sharp particle diameter distribution and stability
15 of dispersion.

[0053]

An oil phase, in which the toner composition is dispersed, is
emulsified and dispersed in a liquid containing water by using a
dispersing agent. Examples of such dispersing agent may include
20 anion surfactants such as alkylbenzene sulfonate, α -olefin
sulfonate, and phosphoric ester; cationic surfactants including
amine salt surfactants such as alkylamine salt, amino alcohol fatty
acid derivatives, polyamine fatty acid derivatives, and imidazolin;
cationic surfactants including quaternary ammonium salt
25 surfactants such as alkyltrimethyl ammonium salt, dialkyldimethyl
ammonium salt, alkyl dimethylbenzyl ammonium salt, pyridinium salt,
alkyl isoquinolinium salt, benzenethonium chloride; nonionic
surfactants such as fatty acid amide derivatives and polyhydric
alcohol derivatives; and amphoteric surfactants such as alanine,
30 dodecyl (aminoethyl) glycine, di (octylaminoethyl) glycine,
N-alkyl-N, N-dimethylammonium betaine, and so forth.

[0054]

Moreover, a surfactant having a fluoroalkyl group is preferable

in that an effect thereof may be attained with only a little usage amount. Examples of suitable anionic surfactant having the fluoroalkyl group may include fluoroalkyl carboxylic acid having carbon atoms of between 2 and 10 and metal salts thereof, disodium
5 perfluorooctane sulfonylglutamate, sodium 3 - [omega - fluoroalkyl (C6 - C11) oxy] - 1 - alkyl (C3 - C4) sulfonate, sodium 3 - [omega - fluoroalkyl (C6 - C8) - N - ethylamino] - 1 - propane sulfonate, fluoroalkyl (C11 - C20) carboxylic acid and metal salts thereof, perfluoroalkyl carboxylic acid (C7 - C13) and metal salts thereof,
10 perfluoroalkyl (C4 - C12) sulfonate and metal salts thereof, perfluorooctanesulfonic acid dietanolamide, N - propyl - N - 2 - hydroxyethyl perfluorooctane sulfonamide, perfluoroalkyl (C6 - C10) sulfonamide propyltrimethylammonium salt, perfluoroalkyl (C6 - C10) - N - ethylsulfonyl glycine salt, monoperfluoroalkyl (C6
15 - C16) ethylphosphate, and so forth.

[0055]

Examples of commercially available products thereof are Surflon S-111, S-112, S-113 (manufactured by Asahi Glass Co., Ltd.), Fluorad FC-93, FC-95, FC-98, FC-129 (manufactured by Sumitomo 3M Limited),
20 UNIDAYNE DS-101, DS-102 (manufactured by Daikin Industries, Ltd.), MEGAFACE F-110, F-120, F-113, F-191, F-812, F-833 (manufactured by Dainippon Ink and Chemicals Incorporated), Ektop EF-102, 103, 104, 105, 112, 123A, 123B, 306A, 501, 201, 204 (manufactured by Tohkem Products Corporation), and Ftergent F-100, F-150
25 (manufactured by Neos Co., Ltd.), and so forth.

[0056]

Examples of the cationic surfactant may include primary, secondary or secondary aliphatic amines having a fluoroalkyl group, quaternary ammonium salts of fatty acids such as perfluoroalkyl
30 (C6 to C10) sulfonamide propyltrimethylammonium salt, benzalkonium chloride, benzethonium chloride, pyridinium salt, and imidazolinium salt. Commercially available products may include, for instance, Surflon S-121 (manufactured by Asahi Glass Co., Ltd.),

Fluorad FC-135 (manufactured by Sumitomo 3M Limited), UNIDAYNE DS-202 (manufactured by Daikin Industries, Ltd.), MEGAFACE F-150, F-824 (manufactured by Dainippon Ink and Chemicals Incorporated), and Ftergent F-300 (manufactured by Neos Co., Ltd.), and so forth.

5 [0057]

In addition, water-insoluble inorganic compound may also be used as a dispersing agent. Examples of such compound are tricalcium phosphate, calcium carbonate, titanium oxide, colloidal silica, hydroxyapatite, and so forth.

10 [0058]

In addition, polymeric protecting colloid may be used to stabilize dispersion drops. Examples of the polymeric protecting colloid may include acids such as an acrylic acid, an methacrylic acid, an α - cyanoacrylic acid, an itaconic acid, an crotonic acid, 15 an fumaric acid, and a maleic acid; (meth)acrylic monomer having a hydroxyl group such as a beta -hydroxyethyl acrylic acid, a beta -hydroxyethyl methacrylic acid, a beta -hydroxypropyl acrylic acid, a beta -hydroxypropyl methacrylic acid, a γ - hydroxypropyl acrylic acid, a γ - hydroxypropyl methacrylic acid, a 3-chloro 2 - 20 hydroxypropyl acrylic acid, a 3 - chloro 2 - hydroxypropyl methacrylic acid, diethyleneglycol monoacrylic ester, diethyleneglycol monomethacrylic ester, glycerin monoacrylic ester, glycerin monomethacrylic ester, N-methylolacrylamide, N-methylolmethacrylamide, and the like; vinyl alcohol or ethers 25 with vinyl alcohol such as vinylmethylether, vinylethylether, vinylpropylether, or the like; esters of a compound having vinyl alcohol and a carboxyl group such as vinyl acetate, vinyl propionate, and vinyl lactate; acrylamide, methacrylamide, diacetoneacrylamide, and methylol compounds thereof; acid 30 chlorides such as acryl chloride, methacryl chloride, or the like; homopolymers or co-polymers having a nitrogen atom or its heterocyclic ring, such as vinyl pyridine, vinyl pyrrolidone, vinyl imidazole, and ethylene imine; polyoxyethylenes such as

polyoxyethylene, polyoxypropylene, polyoxyethylene alkylamine, polyoxypropylene alkylamine, polyoxyethylene alkylamide, polyoxypropylene alkylamide, polyoxyethylene nonylphenylether, polyoxyethylene laurylphenylether, polyoxyethylene stearic phenylester, and polyoxyethylene nonylphenylester; and celluloses such as methyl cellulose, hydroxymethyl cellulose, hydroxypropyl cellulose.

[0059]

In order to remove an organic solvent from the obtained emulsified dispersion, the whole part thereof may be gradually heated so as to completely evaporate and remove the organic solvent in a vapor drop. It is also possible to completely remove the non-soluble organic solvent in the vapor drop by spraying the emulsified dispersion into a dry atmosphere so as to form a toner fine particle. In this case, the aqueous dispersing agent can also be evaporated and removed together with the organic solvent. Examples of the dry atmosphere are heated gases such as air, nitrogen, carbon dioxide, and combustion gas. Draft of the above-mentioned gases which is heated at higher temperature than the highest boiling point of the used solvents is generally used. A targeting quality is efficiently achieved with a high-speed treatment such as using a spray dryer, a belt dryer, and a rotary kiln.

[0060]

When a material soluble in acid such as calcium phosphate or in alkali is used a dispersing stabilizer, acid such as hydrochloric acid is applied for dissolving calcium phosphate, and so forth, and thereafter the particles are subjected to rinse with water so as to remove calcium phosphate from the particle. Further, enzymes or the like may also be used to decompose the dispersing stabilizer so as to remove the dispersing stabilizer from the particle.

[0061]

In a case that the dispersing agent is used, the dispersing agent may be left on a surface of toner particle. However, it is

preferable to wash the dispersing agent off after elongation and/or cross-linking reaction from a viewpoint of charging ability of the toner.

A solvent, which may dissolve the urea-modified polyester (u) or the (A), may also be used to lower viscosity of the toner composition. It is preferred to use the solvent in terms of sharp particle diameter distribution. Moreover, the solvent preferably has a boiling point of less than 100 °C and exhibits volatility from a viewpoint of ease of elimination. Examples of the solvent are toluene, xylene, benzene, carbon tetrachloride, methylene chloride, 1, 2 - dichloroethane, 1, 1, 2 - trichloroethane, chloroform, monochlorobenzene, dichloroethylidene, methyl acetate, ethyl acetate, methylethylketone, methylisobutylketone, and so forth. These may be used singly or in combination of two or more. Of these, particularly preferable solvents are aromatic solvents such as toluene and xylene, and halogenated hydrocarbons such as methylene chloride, 1, 2 - dichloroethane, chloroform, and carbon tetrachloride. The usage amount of the solvent is generally between 0 and 300 parts by weight, preferably between 0 and 100 parts by weight, and more preferably between 25 and 70 parts by weight, relative to 100 parts by weight of the pre-polymer (A). In order to remove the solvent, the solvent is heated under normal pressure or reduced pressure after the elongation and/or the cross-linking reaction.

[0062]

The reaction time of the elongation and/or the cross-linking reaction is selected according to the reactivity of a combination of an isocyanate group structure within the pre-polymer (A) and the amines. The reaction time is generally between 10 minutes and 40 hours, and preferably between 2 and 24 hours. The reaction temperature is generally between 0 and 150 °C, and preferably between 40 and 98 °C. Additionally, publicly-known catalysts may be used, if required. Examples of the catalyst are dibutyltin

laurate, dioctyltin laurate, and so forth.

[0063]

In order to remove an organic solvent from the obtained emulsified dispersion, the whole part thereof may be gradually heated so as to completely evaporate and remove the organic solvent in a vapor drop. It is also possible to completely remove the non-soluble organic solvent in the vapor drop by spraying the emulsified dispersion into a dry atmosphere so as to form a toner fine particle. In this case, the aqueous dispersing agent can also be evaporated and removed together with the organic solvent. Examples of the dry atmosphere are heated gases such as air, nitrogen, carbon dioxide, and combustion gas. Draft of the above-mentioned gases which is heated at higher temperature than the highest boiling point of the used solvents is generally used. A targeting quality is efficiently achieved with a high-speed treatment such as using a spray dryer, a belt dryer, and a rotary kiln.

If a particle size distribution is wide at the time of emulsified dispersion, and washing and drying processing is performed while keeping the particle size distribution, the particles are graded so as to achieve the desired particle size distribution.

[0064]

The grading of particles may be carried out in the solution using a cyclone, a decanter, centrifugal, and so forth, so as to remove a fine particle part. Although the grading may be carried out on dried particles after drying, it is preferable to perform the grading in a solution from a viewpoint of efficiency of the process. The obtained unwanted irregular particles or coarse particles may be sent back to the kneading process to be used in formation of the particles. In this case, the fine particles or the coarse particles may be in a wet condition.

The dispersing agent is preferably removed from the obtained dispersion liquid, and more preferably removed at the same time of the grading mentioned above.

[0065]

The obtained dried toner particles are mixed with other particles such as a mold-releasing agent particle, a charge control particle, a superplasticizer particle, and a colorant particle. Thereafter, mechanical impact force is applied to the mixed particles so as to fix or fuse the particles on the surface of the toner particle. In this way, other particles may be prevented from being removed from a surface of the obtained complex particle.

[0066]

Specific means for applying impact force are, for example, a method in which the impact force is applied to the mixed particles by using a impeller blade rotating in high speed, a method of placing the mixed particles in high-speed flow so as to cause the mixed particles or complex particles to collide with a suitable collision board. Examples of the apparatus may include an angmill (manufactured by Hosokawa Micron Corporation), a modified I-type mill (manufactured by Nippon Pneumatic MFG, Co., Ltd) of which pulverizing air pressure is reduced, a hybridization system (manufactured by Nara Machine Corporation), a Krypton System (manufactured by Kawasaki Heavy Industries, Ltd.), an automatic mortar, and so forth.

[0067]

A volume average particle diameter (D_v) of the toner according to the present invention is between 3 and 8 μm , and the ratio (D_v/D_n) of number average particle diameter (D_n) to the volume average particle diameter (D_v) is between 1.00 and 1.20. It is preferable that the volume average particle diameter (D_v) is between 3 and 6 μm and the ratio D_v/D_n is between 1.00 and 1.15 from viewpoints of excellent heat resistant storage stability, low temperature fixing ability, and hot offset resistance of the dry toner. Especially glossiness of an image becomes excellent in a case that the toner is used in a full-color copier. Further, in a case that the toner is used as a two component developer, variation of the

toner particle diameter is minimized even when consumption and addition of the toner is repeatedly performed in a development device for a long period of time, and favorable and stable developability may be achieved, accordingly. In a case that the toner is used as a one component developer, not only the variation of the toner particle diameter is minimized, but also filming of the toner to a developing roller, and toner fusion of a member such as a toner blade for thinning a layer of the toner are also prevented. Hence, even when the toner is used (stirred) in the development device for a long period of time, stable and excellent developability and images may be obtained.

[0068]

It is generally said that the smaller a toner diameter is, the more advantageous to obtain higher image resolution and image quality. On the other hand, the toner having a smaller toner diameter is disadvantageous in transferability and cleaning ability. When a volume average particle diameter of the toner is smaller than the diameter according to the present invention, in a case of a two component developer, the toner is prone to fuse onto a surface of carrier by being stirred in the development device for a long period of time, lowering charging ability of the carrier. When a single-component developer is used as the toner, toner filming to a developing roller and toner fusion to a member such as a blade for thinning a layer of the toner are likely to occur.

[0069]

These phenomena are largely related to a content of fine particles. If a toner contains toner particles having a diameter of $3\ \mu\text{m}$ or less at more than 10 % by number relative to the total number thereof, the toner is more likely to adhere onto the carrier. Therefore, a problem occurs when stability of charge is highly required.

[0070]

On the other hand, when a particle diameter of toner is larger than a size according to the present invention, not only it is hard

to obtain an image of high resolution and high quality, but also the toner particle diameter often varies largely when the toner is consumed and supplied during developing. In addition, when the ratio D_v/D_n is 1.20 or more, resolution tends to be lowered. When the toner particle diameter is 3 μm or less, suspended toner particles may harm a human body. When the toner particle diameter is 8 μm or more, sharpness of toner image on a photoconductor is decreased, hence an image resolution is decreased.

[0071]

An average particle diameter and a particle size distribution of toner are measured by a coulter counter method. Measuring devices according to the coulter counter method may include a Coulter Counter TA-II and a Coulter Multisizer II (manufactured by Beckman Coulter, Inc.). In the present invention, an average particle diameter and a particle diameter distribution of a toner are measured by using the Coulter Counter TA-II connected with a personal computer PC 9801 (manufactured by NEC Corporation) in which an Inter Face (manufactured by Institute of Japanese Union of Scientists & Engineers) is installed. The Inter Face is capable of analyzing and outputting a number distribution and a volume distribution of toner.

[0072]

The circularity of the dry toner according to the present invention is measured by using a flow-type particle image analyzer FPIA-2000 (manufactured by Sysmex Corporation).

[0073]

The average circularity of the dry toner according to the present invention is in a range of between 0.93 and 1.00. It is very important for the toner according to the present invention to have a certain shape and a certain distribution of the shape. When an average circularity of the toner is less than 0.93 and the shape of the toner particle is too amorphous to be a round shape, sufficient transferability or a high quality image without dust may not be

obtained. The toner having amorphous shape has stronger adhesion force such as van der Waals force and image force than a relatively spherical particle because the toner has more contact points a smooth medium such as a photoconductor, and charges tend to be concentrated in the concave portions. Accordingly, in an electrostatic transferring process, in the toner formed of a mixture of an amorphous particle and a spherical particle, the particle having a spherical shape are selectively moved, resulting in a hollow defect in a character part or a line image part. In addition, there are also problems in that the remained toner is to be removed for a next a toner yield (a usage ratio of the toner for image formation) is low. A circularity of the pulverized toner is generally 0.910 to 0.920. Specific measuring method of the circularity is explained later.

[0074]

When the toner according to the present invention used in a two component developer, the toner is mixed with a magnetic carrier. The toner content in the double-component developer is 1 to 10 parts by weight relative to 100 parts by weight of the magnetic carrier. The magnetic carrier may be selected from any publicly-known carriers such as an iron particle, a magnetite particle, or a magnetic resin carrier, having a particle diameter of 20 to 200 μ m. Coating materials may include an amino resin such as a urea-formaldehyde resin, a melamine resin, a benzoguanamine resin, a urea resin, a polyamide resin, an epoxy resin, and so forth. Another examples are polyvinyl or polyvinylidene resins such as a acrylic resin, a polymethylmethacrylate resin, a polyacrylonitrile resin, a polyvinyl acetate resin, a polyvinyl alcohol resin, and a polyvinylbutyral resin; polystyrene resins such as a polystyrene resin and a styrene-acryl copolymer resin; halogenated olefin resins such as polyvinyl chloride or the like; polyester resins such as a polyethyleneterephthalate resin and a polybutyleneterephthalate resin; a polycarbonate resin, a

polyethylene resin, a polyvinyl fluoride resin, a polyvinylidene fluoride resin, a polytrifluoroethylene resin, a polyhexafluoropropylene resin, a copolymer of vinylidene fluoride and acryl monomer, a copolymer of vinylidene fluoride and vinyl fluoride, fluoro terpolymers such as terpolymer of tetrafluoroethylene, vinylidene fluoride, and non-fluoride monomer, a silicone resin, and the like. Further, an electroconductive particle, and so forth, may be added in a coating resin, if required. Examples of the electroconductive particles are metal particles, carbon black, titanium oxide, tin oxide, zinc oxide, and so forth. The electroconductive particle preferably has an average particle diameter of 1 μm or less. If the average particle diameter is more than 1 μm , it is hard to control electric resistance. The toner according to the present invention may also be suitably used as one component magnetic toner or non-magnetic toner.

[0075]

Fig. 1 is a schematic diagram illustrating a fixing device of the image forming apparatus according to the present invention. In Fig. 2, reference numerals 1, 2, 3, 4, 5, 6, 7, 8, T, and S indicate a fixing roller, a pressing roller, a metal cylinder, an offset inhibiting layer, a heating lamp, a metal cylinder, an offset inhibiting layer, a heating lamp, a toner image, and a support body (transfer paper such as a sheet), respectively.

In the fixing device of the image forming apparatus according to the present invention, conventionally, fixing is not performed with the surface pressure (roller load/contact area) applied on the nip between the two rollers of 1.5×10^5 Pa or less. Conventionally, the surface stress is more than 1.5×10^5 Pa, otherwise fixing becomes insufficient. On contrary, the toner according to the present invention is capable of fixing at low temperature so that it is possible to perform fixing with the surface stress of 1.5×10^5 Pa or less. By performing fixing with low surface

stress, a toner image is not pushed onto the recording medium and thus a high definition image may be output.

[0076]

[Embodiment]

5 The present invention is further explained according to the following embodiments. However, the present invention is not limited to the embodiments. In the embodiments, part(s) indicates part(s) by weight.

[0077]

10 Embodiment 1

(Synthesis of toner binder)

724 parts of bisphenol A ethylene oxide bimolar adduct, 276 parts of isophthalic acid and 2 parts of dibutyl tin oxide are introduced into a reaction vessel equipped with a condenser tube, a stirrer, and a nitrogen inlet tube, are reacted under normal pressure at 15 230 °C for 8 hours, are reacted again for 5 hours by decreasing pressure for 10 to 15 mmHg and are cooled to 160 °C. Then 32 parts of phthalic anhydride are added and the reaction is continued for 2 another hours. Next, the reaction mixture is cooled to 80°C, and 20 188 parts of isohorone diisocyanate is added in ethyl acetate and reacted for 2 hours to obtain pre-polymer (A) containing isocyanate. Next, 267 parts of the pre-polymer (A) and 14 parts of isohorone diamine are reacted at 50 °C for 2 hours to obtain a urea-modified polyester resin (u) having a weight average molecular weight of 25 64000. Similarly to the above, 724 parts of bisphenol A ethylene oxide bimolar adduct and 276 parts of terephthalic acid are subjected to polycondensation at 230 °C for 8 hours, and are reacted for 5 hours by decreasing pressure for 10 mmHg to 15mmHg to obtain non-modified polyester (a) having a peak molecular weight of 5,000. 30 200 parts of the urea-modified polyester resin (1) and 800 parts of the non-modified polyester resin (a) are dissolved and mixed in 2,000 parts of ethyl acetate/MEK (1/1) mixed solvent to obtain an ethyl acetate/MEK solution of the toner binder (1). The

resulting mixture is dried under partially reduced pressure to isolate the toner binder (1). In this case, T_g is 62°C , an acid value is 4.2 KOHmg/g, and a peak molecular weight is 4,500.

[0078]

5 (Production of toner)

240 parts of an ethyl acetate/MEK solution of the toner binder (1), 5 parts of ester wax as wax (acid value: 3) and 8 parts of carbon black (BP1300, manufacturer: Cabot Corporation) are introduced into a beaker, and stirred at 12,000 rpm at 60°C by a
10 TK homomixer to uniformly dissolve and disperse the ingredients. 706 parts of ion exchange water, 294 parts of a 10% suspension of hydroxyapatite (Supertite 10, manufacture: Japan Chemical Industries) and 0.2 parts of a sodium dodecyl benzene sulfonate are introduced into the beaker, and are uniformly dissolved. Next,
15 the temperature is raised to 60°C , and the above toner material solution is introduced while stirring at 12,000 rpm by the TK homomixer for 10 minutes. Then, the solution is left to stand for 2 hours for stabilization. Next, the mixed solution is transferred to a flask equipped with a stirring rod and a thermometer, and the
20 temperature is raised to 98°C to remove the solvent. Subsequently, the product is filtered, rinsed, and dried, and then graded by air power to obtain toner particles having an average particle diameter of $6.3\ \mu\text{m}$ (volume average particle diameter D_v /number average particle diameter D_n : 1.14), and a circularity of 0.97. Next, 0.5
25 parts of hydrophobic silica and 0.5 parts of hydrophobic titanium oxide are added to 100 parts of the toner particles and mixed in a Henschel mixer to obtain the toner (1) according to the present invention. In the toner, an occupied area ratio of the wax in an area from a surface of toner particle to a $1\ \mu\text{m}$ inner area is 20
30 (%), the wax not existing on the surface of the toner particle but existing adjacent to the surface of the toner particle are 86 % by number, and the wax particles having a dispersion diameter of

0.1 to 3.0 μm are 88 % by number. An evaluation result is shown in Table 1.

[0079]

Embodiment 2

5 (Synthesis of toner binder)

Similar to the embodiment 1, 334 parts of bisphenol A ethylene oxide bimolar adduct, 334 parts of bisphenol A propylene oxide bimolar adduct, 274 parts of isophthalic acid, and 20 parts of anhydrous trimellitic acid are subjected to polycondensation, and
10 then reacted with 154 parts of isohorone diisocyanate to obtain a pre-polymer (2). Next, 213 parts of the prepolymer (2), 9.5 parts of isohorone diamine and 0.5 parts of dibutylamine are reacted in the same way as in the embodiment 1 to obtain urea-modified polyester (2) having a weight average molecular weight of 52,000. 200 parts
15 of the urea-modified polyester (2) and 800 parts of the non-modified polyester (a) are dissolved and mixed in 2,000 parts of ethyl acetate/MEK (1/1) mixed solvent, to obtain an ethyl acetate solution of the toner binder (2). A part of the solution is dried under reduced pressure to isolate the toner binder (2). T_g is 65°C, the
20 acid value is 10, and the peak molecular weight is 5500.

[0080]

(Production of toner)

The identical procedure as the procedure of the embodiment 1 is used except that the ester wax is replaced by 7 parts of de-free
25 fatty acid carnauba wax (acid value: 1.5) and is used as wax, and the dissolution temperature and dispersion temperature are changed to 50 °C to obtain the toner (2) according to the present invention having a particle diameter of 5.8 μm (D_v/D_n : 1.11) and a circularity of 0.98. In the toner, an occupied area ratio of the wax in an area
30 from a surface of toner particle to a 1 μm inner area is 30 (%), the wax not existing on the surface of the toner particle but existing adjacent to the surface of the toner particle are 79 % by number, and the wax particles having a dispersion diameter of 0.1 to 3.0

μm are 90 % by number. An evaluation result is shown in Table 1.

[0081]

Comparative example 1

(Synthesis of toner binder)

5 354 parts of bisphenol A ethylene oxide bimolar adduct and 166 parts of isophthalic acid are subjected to polycondensation using 2 parts of dibutylene oxide as a catalyst to obtain a comparative toner binder (1) having a weight average molecular weight of 8,000. Tg, an acid value, and a peak molecular weight the comparative toner
10 binder (1) are 57 °C, 15, and 6000, respectively.

[0082]

(Production of toner)

100 parts of the toner binder (1), 200 parts of an ethyl acetate solution, 10 parts of carbon black (BP1300, manufacturer: Cabot
15 Corporation), and 10 parts of polypropylene are introduced into a beaker, and stirred at 12,000 rpm at 50 °C by a TK homomixer to uniformly dissolve and disperse the ingredients. Then the toner is prepared in the same manner as in the embodiment 1. Thus comparative toner (1) having a volume average particle diameter
20 of 6.0 μm (Dv/Dn: 1.36) and a circularity of 0.95 is obtained. In the toner, an occupied area ratio of the wax in an area from a surface of toner particle to a 1 μm inner area is 3 (%), the wax not existing on the surface of the toner particle but existing adjacent to the surface of the toner particle are 55 % by number, and most part
25 of the rest of the wax particles exists inner part of the particle. The wax particles having a dispersion diameter of 0.1 to 3.0 μm are 63 % by number. An evaluation result is shown in Table 1.

[0083]

[Table 1]

	Occupied area ratio of the wax in an area from a surface of toner	Particle fluidity	Lowest fixing temperature	Hot (°C)	Heat resistant storage stability
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	particle to a 1 μ m inner area (%)		(°C)		
Emb. 1	20%	0.27	110 °C	210 °C	○
Emb. 2	30%	0.25	120 °C	230 °C or more	⊙
Com. 1	3%	0.27	140 °C	170 °C	△

[0084]

Embodiment 3

(Production example of pre-polymer)

5 724 parts of bisphenol A ethylene oxide bimolar adduct, 250 parts of isophthalic acid, 24 parts of terephthalic acid, and 2 parts of dibutylene oxide are introduced in a reaction vessel equipped with a condenser tube, a stirrer, and a nitrogen supply tube. Then the ingredients are reacted at 230 °C under normal pressure for 8
10 hours. Thereafter, the resulted mixture is further reacted under a reduced pressure of 10 mmHg to 15 mmHg for 5 hours while dewatering. The reaction mixture is then cooled to 160 °C and 32 parts of phthalic anhydride is added in the reaction mixture to react for 2 hours. The reaction mixture is further cooled to 80°C, and is reacted with
15 188 parts of isophorone diisocyanate in ethyl acetate for 2 hours. A pre-polymer (3) containing an isocyanate group having a weight average molecular weight of 12000 is thus produced.

[0085]

(Production example of Ketimine compound)

20 30 parts of isophorone diamine and 70 parts of methylethyl ketone are introduced into a reaction vessel equipped with a stirring rod and a thermometer, and then reacted at 50 °C for 5 hours to obtain a ketimine compound (1).

[0086]

(Production example of non-modified polyester)

Similar to the above, 724 parts of bisphenol A ethylene oxide bimolar adduct and 276 parts of terephthalic acid are subjected to polycondensation at 230 °C under normal pressure for 6 hours.

5 Thereafter, the resulted mixture is further reacted under a reduced pressure of 10 mmHg to 15 mmHg for 5 hours while dewatering. Thus the non-modified polyester (b) having a peak molecular weight of 6000 and an acid value of 3.8 is obtained.

[0087]

10 (Production example of toner)

15 15.4 parts of the pre-polymer (1), 64 parts of the polyester (b) and 78.6 parts of ethyl acetate are introduced into a beaker, and then the ingredients are stirred and dissolved. Next, 8 parts of rice wax functioning as wax, and 4 parts of copper phthalocyanine blue are added and stirred at 12,000 rpm at 60 °C by a TK homomixer to uniformly dissolve and disperse the ingredients. Then, 2.7 parts of the ketimine compound (1) is added and dissolved to obtain a toner material solution (1). 706 parts of ion exchange water, 294 parts of a 10% suspension of hydroxyapatite (Supertite 10, 20 manufacture: Japan Chemical Industries) and 0.2 parts of a sodium dodceyl benzene sulfonate are introduced into the beaker, and are uniformly dissolved. Next, the temperature is raised to 60°C, and the above toner material solution (1) is introduced while stirring at 12,000 rpm by the TK homomixer for 10 minutes. Thereafter, the 25 mixed solution is left to stand for 2 hours to stabilize. Next, the mixed solution is transferred to a flask equipped with a stirring rod and a thermometer, and the temperature is raised to 98 °C to remove the solvent by causing a urea reaction. Subsequently, the product is filtered, rinsed, and dried, and then graded by air power 30 to obtain toner particles having an average particle diameter of 4.3 μm. Next, 0.5 parts of hydrophobic silica and 0.5 parts of hydrophobic titanium oxide are added to 100 parts of the toner particles and mixed in a Henschel mixer to obtain the toner (5)

according to the present invention. (D_v/D_n : 1.08), circularity 0.94, peak molecular weight 6000, and T_g 62 °C are obtained. In the toner, an occupied area ratio of the wax in an area from a surface of toner particle to a 1 μ m inner area 20 (%), the wax not existing on the surface of the toner particle but existing adjacent to the surface of the toner particle are 90 % by number, and the wax particles having a dispersion diameter of 0.1 to 3.0 μ m are 88 % by number. An evaluation result is shown in Table 3.

[0088]

10 Embodiment 4

(Production example of prepolymer)

Similar to the embodiment 1, 669 parts of bisphenol A ethylene oxide bimolar adduct, 274 parts of isophthalic acid, and 20 parts of trimellitic anhydride are subjected polycondensation, and thereafter the resulted product is reacted with 154 parts of isophorone diisocyanate to obtain pre-polymer (4) having a volume average molecular weight of 15,000.

[0089]

(Production example of toner)

20 15.5 parts of the pre-polymer (2), 64 parts of polyester (b) and 78.8 parts of ethyl acetate are introduced into a beaker, and are stirred and dissolved. Next, 5 parts of montan wax functioning as wax, and 4 parts of copper phthalocyanine blue are added and stirred at 12,000 rpm at 50 °C by a TK homomixer to uniformly dissolve and disperse the ingredients. Finally, 2.4 parts of the ketimine compound (1) and 0.036 parts of dibutyl amine are added and dissolved to obtain a toner material solution (2). The identical procedure as the procedure in the embodiment 3 is used except that the toner material solution (1) is replaced by the toner material solution (2), and the dispersion temperature is changed to 50 °C to obtain the toner (6) according to the present invention having a volume average particle diameter of 7.2 μ m (D_v/D_n : 1.15), and a circularity of 0.98. In the toner, an occupied area ratio of the

wax in an area from a surface of toner particle to a 1 μm inner area is 25 (%), the wax not existing on the surface of the toner particle but existing adjacent to the surface of the toner particle are 92 % by number, and the wax particles having a dispersion diameter of 0.1 to 3.0 μm are 94 % by number. Tg is 60 $^{\circ}\text{C}$ and the peak molecular weight is 4000. An evaluation result is shown in Table 2.

[0090]

Comparative example 2

(Synthesis of toner binder)

354 parts of bisphenol A ethylene oxide bimolar adduct and 166 parts of terephthalic acid are subjected to polycondensation using 2 parts of dibutylene oxide as a catalyst to obtain a comparative toner binder (2) having a peak molecular weight of 8,000.

[0091]

(Production example of toner)

100 parts of the comparative toner binder (2), 200 parts of an ethyl acetate, 4 parts of copper phthalocyanine blue, and 5 parts of polypropylene are introduced into a beaker, and stirred at 12,000 rpm at 50 $^{\circ}\text{C}$ by a TK homomixer to uniformly dissolve and disperse the ingredients. Thus a comparative toner material solution is obtained. Thereafter, the toner is produced in the same manner as in the embodiment 4, and comparative toner (2) having a volume average particle diameter of 6.9 μm (Dv/Dn: 1.45) and a circularity of 0.94 is obtained. In the toner, an occupied area ratio of the wax in an area from a surface of toner particle to a 1 μm inner area is 45 (%), the wax not existing on the surface of the toner particle but existing adjacent to the surface of the toner particle are 65 % by number, and most part of the rest of the wax particles are exposed on the surface of the toner the particles. The wax particles having a dispersion diameter of 0.1 to 3.0 μm are 68 % by number. An evaluation result is shown in Table 3.

[0092]

[Table 2]

	Occupied area ratio of the wax in an area from a surface of toner particle to a 1 μ m inner area (%)	Particle fluidity	Lowest fixing temperature (°C)	Hot (°C)	Heat resistant storage stability
Emb. 3	20%	0.26	130 °C	220 °C	○
Emb. 4	25%	0.29	120 °C	230 °C or more	◎
Com. 2	45%	0.16	150 °C	230 °C or more	×

[0093]

(Measuring method)

5 (1) Particle diameter distribution

At first, 0.1 to 5 ml of a surfactant (preferably alkylbenzene sulfonate) functioning as a dispersant is added to 100 to 150 ml of an electrolytic solution. The electrolytic solution is prepared from 1 % NaCl solution of primary sodium chloride. In this case, for example, ISOTON-II (manufacturer: Beckman Coulter, Inc.) may be used. Further, 2 to 20 mg of a test portion is added to the electrolytic solution. The electrolytic solution suspending the test portion is dispersed by an ultrasonic disperser for about 1 to 3 minutes. Thereafter, toner particles or toner volume, number of toner are measured by the above-mentioned measuring apparatus using an aperture of 100 μ m. Thus a volume particle distribution and number particle distribution are calculated.

[0094]

As channels, 13 channels of between 2.00 and less than 2.52 μ

m, between 2.52 and less than 3.17 μm , between 3.17 and less than 4.00 μm , between 4.00 and less than 5.04 μm , between 5.04 and less than 6.35 μm , between 6.35 and less than 8.00 μm , between 8.00 and less than 10.08 μm , between 10.08 and less than 12.70 μm , between 12.70 and less than 16.00 μm , between 16.00 and less than 20 μm , between 20.20 and less than 25.04 μm , between 25.40 and less than 32.00 μm , and between 32.00 and less than 40.30 μm are used. A particle having a particle diameter of 2.00 or more to less than 40.30 μm are applied. A ratio D_v/D_n is calculated from a volume average particle diameter (D_v) of volume reference obtained from the volume particle distribution relating to the present invention, and a number average particle diameter (D_n) obtained from the number particle distribution.

[0095]

(2) Circularity

An optical detection band method suitable a method of measuring a shape. In the method, particle-containing suspension is passed through a photographic detection band on a plate, and a particle image is optically detected by/analyzed with a CCD camera. It is found that the toner having an average circularity of 0.960 or more may be effective in forming a high-resolution image with appropriate density reproducibility. The average circularity of 0.960 is obtained by the method by dividing a circumference length of a circle having a substantially equal projected area by a circumference length of an existing particle, and the toner having the average circularity of 0.980 or more is determined to be effective to form a high definition image with appropriate reproducibility and toner density. The toner is preferably have an average circularity of 0.980 to 1.000. The value is measured as the average circularity by a flow type particle image analyzer FPIA-2000. Specifically, 0.1 to 5 ml of a surfactant, preferably alkylbenzene sulfonate, functioning as a dispersant is added to 100 to 150 ml of water in

a vessel in which a solid impurity is removed beforehand. Further, 0.1 to 0.5 g of a test portion is added to the water. The suspension in which the test portion is dispersed is subjected to dispersal processing for about 1 to 3 minutes by the ultrasonic disperser. In this case, the concentration of the dispersion liquid is set to 3000 to 10000 number/ μ l, and the shape and the distribution of the toner is measured by the apparatus.

[0096]

(3) Particle fluidity

Powder density of the toner is measured by using a Powder Tester (manufacture: Hosokawa Micron Corporation). The better fluidity of toner is, the more powder density of the toner is.

[0097]

(4) Lowest fixing temperature ($^{\circ}$ C)

A copying test is carried out on Type-6200 paper manufactured by Ricoh Company, Ltd., by using a modified fixing device of a copier imagio NEO 450 manufactured by Ricoh Company, Ltd., as a fixing roller. The lowest fixing temperature is defined as temperature at which a residual rate of the image density is 70 % or more after rubbing a fixing image with a pad.

A metal cylinder of the fixing roller is formed of a Fe material and has a thickness of 0.34 mm. In addition, a surface pressure is set to 1.0×10^5 PA.

[0098]

(5) Temperature at which hot offset occurs (HOT)

Fixing is evaluated similar to the lowest fixing temperature, and occurrence of hot offset to the fixing image is visually evaluated. The temperature at which the hot offset occurs is defined as temperature of the fixing roller at which the hot offset occurs.

[0099]

(6) Hest-resistant storage stability

Hest-resistant storage stability is defined as a residual rate

of the toner stored at 50 °C for 8 hours and then put through a sifter of a 42 mesh. The better the heat-resistant storage stability, the less the residual ratio is. The heat-resistant storage stability is evaluated using the residual ratio on a scale of one to 10 as follows.

×: 30 % or more

△: 20 to 30 %

○: 10 to 20 %

⊙: less than 10 %

[0100]

[Table 3]

No.	Volume average particle diameter Dv (μm)	Dv/Dn	Average circularity	Tg of toner binder (°C)	Acid value of toner binder (KOHmg)	Peak molecular weight of toner binder
Emb. 1	6.3	1.14	0.97	62	4.2	4500
Emb. 2	5.8	1.11	0.98	65	3.5	5500
Com. 1	6.0	1.36	0.95	57	15.0	6000
Emb. 3	4.3	1.08	0.94	62	2.5	6000
Emb. 4	7.2	1.15	0.98	60	10.0	4000
Com. 2	6.9	1.45	0.94	60	3.0	8000

[0101]

[Table 4]

No.	Wax type (parts by weight)	Occupied area ratio of the wax in an area from a surface of toner particle to a 1 μm inner area	Wax not existing on the surface of the toner particle but existing adjacent to the surface of the	Wax particles having a dispersion diameter of 0.1 to 3.0 μm (by number %)
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		(%)	toner particle (by number %)	
Emb. 1	Ester wax (5)	20	86	88
Emb. 2	Carnauba wax (7)	30	79	90
Com. 1	Polypropylene (10)	3	72	73
Emb. 3	Rice wax (8)	20	90	88
Emb. 4	Montan wax (5)	25	92	94
Com. 2	Polypropylene (5)	45	68	68

[0102]

[Effects of the Invention]

The following effects are achieved by dry toner according to the present invention.

1. In a fixing device of low energy consumption, toner having a wide fixing and releasing width, and excellent storage stability may be achieved.

2. An efficient production method of toner having a wide fixing area and which may achieve a high quality image may be achieved.

3. In a case when the toner is used as color toner, excellent glossiness and hot offset resistance may be achieved. Accordingly, it is not necessary to apply oil on a fixing roller.

4. An image with high-resolution and high-definition may be achieved.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 is a schematic drawing illustrating an example of a fixing device of an image forming apparatus according to the present

invention.

[Reference Numerals]

- 1 Fixing roller
 - 2 Pressing roller
 - 5 3 Metal cylinder
 - 4 Offset inhibiting layer
 - 5 Heating lamp
 - 6 Metal cylinder
 - 7 Offset inhibiting layer
 - 10 8 Heating lamp
 - T Toner image
 - S Support body (transfer paper such as paper)
- [Selected Drawing] None

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[Name of Document] Abstract of the Disclosure

[Abstract]

[Objectives of the Invention] It is an object of the present invention to provide toner which has improved fixing ability at low temperature and offset resistance with low electric power consumption, forms a high quality toner image, and has long-term excellent storage stability.

[Means for Achieving the Objectives] Dry toner comprising at least a toner binder, a colorant, and wax, characterized in that an occupied area ratio of the wax is between 5 and 40 % in an area from a surface of toner particle to a 1 μ m inner area, according to observation by a transmission electron microscope.

[Name of Document]

[Fig. 1]

